

## **Natures Acid Drainage Laboratory: Lessons from the Rötlbach (Zillertaler Alps / Austria)**

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### **Abstract**

The small perennial alpine stream we have investigated drains pyritic schist. It is located in the High Alps and is famous for being the first finding of naturally formed schwertmannite. Changing pH-conditions due to alkaline tributaries lead to the precipitation of a complete succession of secondary iron minerals which can be sampled easily on the barren bed rock. The mineral series starts with iron(III) sulphates at the springs, and encompasses ferrihydrite and goethite as well as the already mentioned sulfoxyhydroxide schwertmannite.

The pH of the main stream stays at relatively low values around 3 - 3.5 which is only slightly higher than the springs, despite the temporarily high inflows of the alkaline tributaries. This is obviously the result of the hydrolysis of iron(III). At the springs the acid drainage also contains up to several hundred micrograms per litre of heavy metals and metalloids. However, metal concentrations are reduced to drinking water standard by the very high adsorption capacities of the precipitated iron minerals.

Even at very low metal concentrations the degree of adsorption (especially for arsenic) to the precipitated iron oxides can lead to concentrations of up to  $6,000 \mu\text{g g}^{-1}$ . This can be as much as 150 times the concentration found in the original source, i.e. the pyrite grains. These high metal loads should be of concern whenever and wherever iron (and/or manganese) precipitates form during the life cycle of a mining project, even when water quality is excellent.

## 1 Introduction

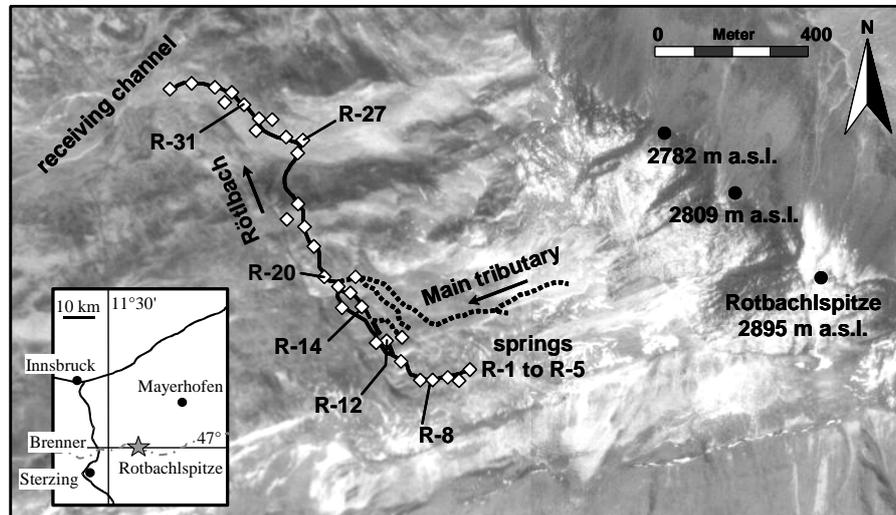
Acid Drainage is not only induced by mining operations, but is a common step in the weathering of rocks containing sulphides. Data from natural occurrences of acid drainage are complimentary to observations from mining projects as they give insight into acidic systems at the geological time scale. Acid drainage often contains high concentrations of metals and metalloids like arsenic, as well as iron, sulphate and protons. The precipitation of iron and the subsequent scavenging of metals onto the precipitates is a well established principle in the use of wetlands (e.g. PIRAMID Consortium 2003).

The small perennial alpine stream called Rötzbach is easily recognized due to its reddish colour indicating the presence of iron precipitates, and was first mentioned in some writings dating back to the second half of the 15<sup>th</sup> century. It became famous for being the first finding of naturally occurring schwertmannite  $\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$  (Schwertmann et al. 1995). Other iron minerals precipitate along the course of the stream, such as sulphates and sulphate free oxides. Study of this sequence of mineral phases can broaden our understanding of how natural geochemical processes can remediate contaminations.

The Rötzbach was sampled during three summers at a maximum of 36 stations. Due to the climate, the springs and the upper part of the Rötzbach were covered with snow until mid July. Following a short snow-free period the temperatures can still drop below zero, before the snows return in October. A major advantage is that the stream flows mostly on barren bed rock, so that no interstitial waters of fine river bed sediments, or interactions of stream water and groundwater by bank filtration have to be accounted for. There are no organic materials in the stream and biological interaction is limited.

## 2 Geology of the area

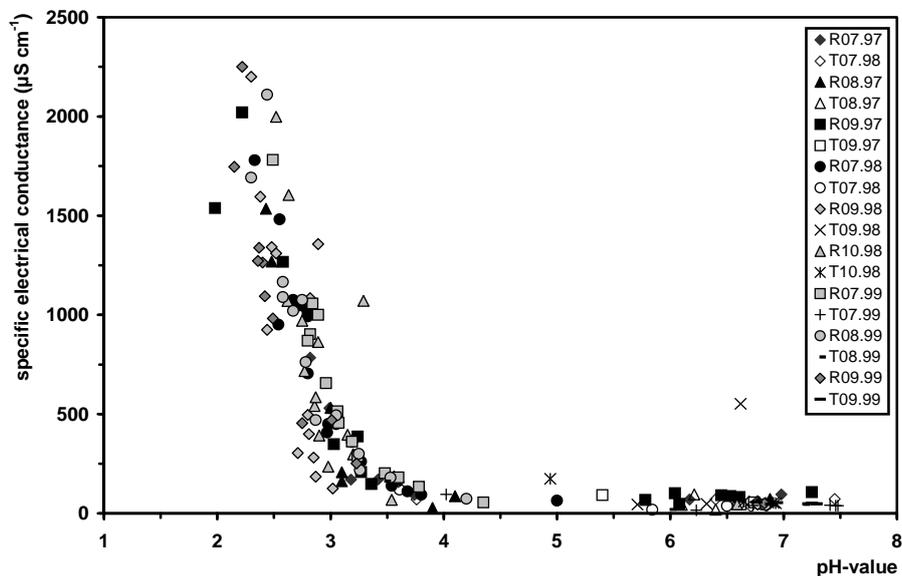
The Rötzbach is located in the western part of the Tauern window in the European Alps at the border between Austria and Italy. The catchment of the springs lies in the western slope of the peak Rotbachlspitze (2895 m a.s.l.). In this part of the Tauern window the two major gneiss cores Tuxer gneiss to the N and Zillertaler gneiss to the S are separated by the Greiner syncline (Lammerer 1988, Lammerer and Weger 1999). The Greiner zone is also interpreted as a major E - W trending shear zone (Behrmann and Frisch 1990, Selverstone 1993).



**Fig. 1.** Aerial photograph of the Rötzbach area (© BEV – 2001, by courtesy of the BEV - Bundesamt für Eich- und Vermessungswesen, Vienna, Zl. 39 821 / 01). Diamonds indicate the sampling points of which a few are mentioned herein

The rocks consist of serpentinites, graphite schists, amphibolites, hornblendegarnen schists, gneisses and muscovite-chlorite schist. The latter contains 4 - 5 % of pyrite up to a few hundred microns in size. The pyrite grains are deformed parallel to the schistosity. Small layers of quartzite with 1 – 2 cm large nests of pyrites occur at the northern ridge of the Rotbachlspitze. There the outcrop of the near vertically dipping rocks is around 100 m in width. The strike of the pyritic schists is  $67^{\circ} - 69^{\circ}$ .

We have measured the hydraulic conductivity  $k_f$  of rock samples parallel and normal to the shear planes in triaxial cells. Samples taken near to the springs of the Rötzbach were prepared as large drill cores with diameters of 0.1 m, which equals an area of  $7.8 \cdot 10^{-3} \text{ m}^2$ . The  $k_f$ -value parallel to the shear planes increases from  $9.5 \cdot 10^{-6} \text{ m s}^{-1}$  at the outer rim of the outcrop of the pyritic schist, to  $1.3 \cdot 10^{-5} \text{ m s}^{-1}$  in the center. Normal to the shear planes we measured, at the rim, a  $k_f$ -value of  $1.2 \cdot 10^{-10} \text{ m}^2$ , which increases to  $8 \cdot 10^{-6} \text{ m}^2$  in the center. The dissolution of silicates has increased the permeability of the rocks, and diminished especially the anisotropy of water flow paths. In the inner zone of the outcrop the pyritic schists are more like an isotropic porous aquifer than a highly layered hard rock. This allows for storage of melt waters in the schists and the preferential flow of groundwaters to the Rötzbach springs.



**Fig. 2.** SC versus pH of the Rötzbach samples (marked R) and its tributaries (marked T) for the three years of sampling

### 3 Hydrochemistry of the Rötzbach

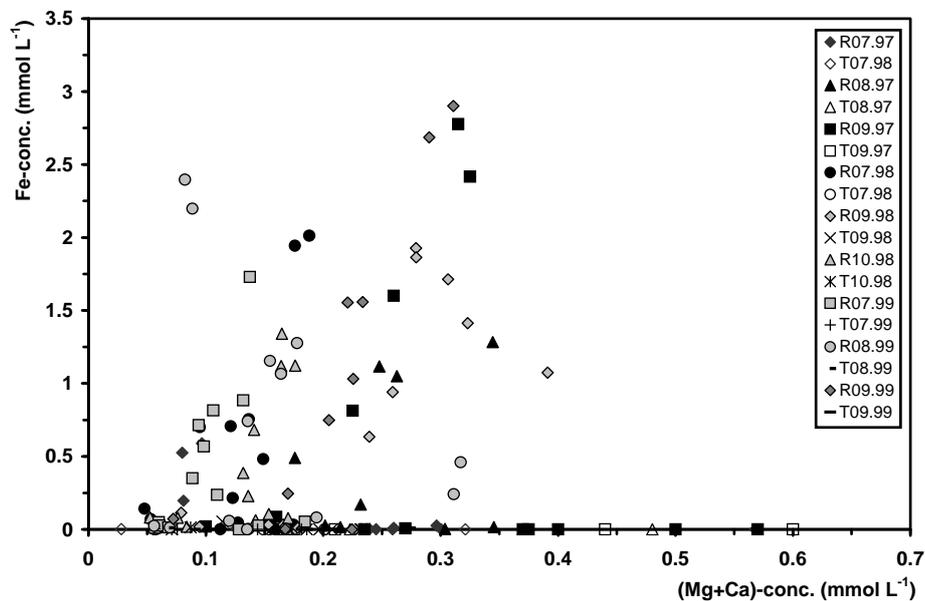
The Rötzbach is the only perennial stream in the area without a feeding glacier. Its subsurface catchment has an area of 30,000 m<sup>2</sup> and the discharge of the springs varies between 1.3 to 4.2 L s<sup>-1</sup>, with an unknown extra discharge during the thaw. Along the first 500 m of the stream, flow increases slowly from small tributaries and diffuse surcharge to around 4 – 11 L s<sup>-1</sup>, depending on the time elapsed since the thaw. Then the main tributary (Fig. 1) increases the flow markedly to 10 – 30 L s<sup>-1</sup>.

The springs of the Rötzbach are acidic (pH ca. 2) with a specific conductance (SC) up to 2,500 µS cm<sup>-1</sup> due to the oxidation of pyrite in the catchments rock. All waters except one are oxidic. The largest spring is suboxic. However, no reduced species of Fe or As were measured indicating the oxidation of ions from pyrite dissolution proceeds to their highest valence states.

The specific conductance decreases along the course to values below 200 µS cm<sup>-1</sup> due to the precipitation of minerals. The release of protons by the formation of iron oxides depresses the pH of the Rötzbach. Only when most of the iron is precipitated will the pH increase to become more like

the basic tributaries. These tributaries are Ca-Mg-HCO<sub>3</sub> type waters with pH values of 6 – 7 and SC values below 50 µS cm<sup>-1</sup> (Fig. 2). The spring waters are dominated by sulphate up to 800 mg L<sup>-1</sup> and iron(III) around 160 mg L<sup>-1</sup>.

Figure 3 shows some relation between Fe(III)- and Mg-Ca-concentrations in the more acidic Rötzbach samples. Iron is correlated with pH and SC, and also with Mg which is the more important one of the two alkaline-earth elements. As discussed about the hydraulic conductivity, these acidic waters have a strong influence on their environment. Their chemistry is the result not only of pyrite oxidation but also of dissolution of bed rock minerals, especially mafic ones.



**Fig. 3.** Fe versus the sum of Mg and Ca of the Rötzbach samples (marked R) and its tributaries (marked T) for the three years of sampling

#### 4 Iron Precipitates

The change in chemistry of the Rötzbach allows for the precipitation of different iron minerals. The mineral jarosite (KFe<sub>3</sub>[(OH)<sub>6</sub>/SO<sub>4</sub>]<sub>2</sub>) precipitates at the main spring which is characterized by the lowest pH and the highest sulphate concentrations, forming a yellow mud of low density. Decreasing sulphate concentration and slightly increasing pH values (3 –

4.5) allow for the formation of schwertmannite, which is the most widely distributed Fe mineral. Along the course schwertmannite is then mixed with goethite; both can, and do form incrustations on the bed rock surface.

#### 4.1 Hydrochemical Environment of the Precipitates

The pH value and sulphate concentration are the most important parameters to control the formation of iron precipitates. The occurrence of jarosite is restricted to the main spring which is at a pH of  $< 2.5$  and sulphate of  $300 \text{ mg L}^{-1}$  during the high flow season, increasing up to  $1000 \text{ mg L}^{-1}$  at the end of the summer period.

Schwertmannite is observed as a precipitate at pH values of 3, to a maximum of 4.3 at one location. The confluence of the Rötlbach with its main tributary (R20, Fig. 1) is marked by a pH of 2.8 – 3.8. Massive precipitation of minerals leads to a 1 cm thick mud of schwertmannite on the rocks at the end of each of the three observed summer periods. Sulphate concentrations are around  $100 - 350 \text{ mg L}^{-1}$  immediately downstream of the springs, and decrease in the zones of highest schwertmannite formation to  $30 - 50 \text{ mg L}^{-1}$ . Downstream of point R20 the values are small, i.e.  $20 - 30 \text{ mg L}^{-1}$ . Thus schwertmannite formation is the major process decreasing the sulphate concentration in the stream.

The decrease in sulphate to below  $100 \text{ mg L}^{-1}$  is accompanied by an increase in goethite formation, forming mixtures with the schwertmannite. It is unclear if the distribution of goethite and schwertmannite reflects temporal fluctuations of pH and sulphate during the year and/or spatial variability of the chemical environment caused by meandering of the stream. It could also indicate the transformation of schwertmannite into goethite with time, as it was observed in laboratory studies (Bigham et al. 1996). With respect to the second process it should be mentioned that As- and Cr-containing schwertmannites did not transform in a laboratory study (Regenspurg et al. 2004).

The low sulphate concentrations downstream of point R20 allow for the formation of sulphate-free iron oxides, as well as schwertmannite. The crystallinity of the minerals is very low. The 2-line ferrihydrite ( $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$ ) is detected at one location (R12). There alkaline waters seep out of the planes of schistosity of the bed rocks and mix with acidic water under varying hydrological conditions. This allows for rapid iron precipitation.

## 4.2 Metal Enrichment

The formation of iron minerals does not only reduce the concentration of sulphate in the acidic waters of the Rötzbach, it has an even more pronounced influence on the concentrations of other metals (As, Co, Ni, Pb for instance). The main spring contains  $> 100 \mu\text{g L}^{-1}$  As, several tens  $\mu\text{g L}^{-1}$  Ni and Pb and  $300 - 1000 \mu\text{g L}^{-1}$  Cu. Immediately downstream of the spring the concentrations of the metals decrease to a few  $\mu\text{g L}^{-1}$  and even below detection limits. Copper is the exception as it stays around  $100 - 300 \mu\text{g L}^{-1}$  until the water reaches R20.

The metals become highly enriched with concentrations far in excess of those present in the parent mineral, i.e. the pyrite. Measurements of trace element concentrations in single pyrite grains give low concentrations of trace metals like arsenic ( $42 \mu\text{g g}^{-1}$ ), lead ( $25 \mu\text{g g}^{-1}$ ) and nickel ( $55 \mu\text{g g}^{-1}$ ). Table 1 shows types of mineral precipitates, and their metal content. Most prominent are the enrichment of arsenic on the oxides, and of lead with regard to jarosites. Enrichment factors are calculated from the source concentrations of the elements in the pyrite and in the precipitates as shown in Table 1.

**Table 1.** Types of iron precipitates (Gt: goethite, Fh: ferrihydrite, Jt: jarosite, Sh: schwertmannite), and concentrations of As, Ni, and Pb in the minerals and in the waters (geometric mean)

	mineral	arsenic		nickel		lead	
		$[\mu\text{g g}^{-1}]$	$[\mu\text{g L}^{-1}]$	$[\mu\text{g g}^{-1}]$	$[\mu\text{g L}^{-1}]$	$[\mu\text{g g}^{-1}]$	$[\mu\text{g L}^{-1}]$
	pyrite	42	---	55	---	25	---
R2	Gt, Jt (Sh)	1239	59.5	184	12.7	170	23.8
R4	Jt	5906	114	60	13.7	3500	42.2
R8	Sh	874	11.9	n.a.	10.5	n.a.	22.6
R12a	Sh, Fh (Gt)	2769		14		50	
R12b	Sh (Gt)	1078	$< 0.5$	n.a.	$< 1.5$	n.a.	$< 1.2$
R14	Sh, Gt	858	5.93	230	1.50	33	7.00
R20	Sh, Gt	304	1.92	46	1.91	100	4.35
R27	Sh, Gt	137	$< 0.5$	n.a.	$< 1.5$	n.a.	1.65
R31	Sh, Gt	446	$< 0.5$	n.a.	n.a.	n.a.	$< 1.2$

As arsenic is very strongly enriched onto the iron oxides, we measured the extended x-ray absorption fine structures (EXAFS) at beam A1 of the Hamburg Synchrotron Radiation Laboratory (HASYLAB, Germany) to learn about the exact mechanism of enrichment. Laboratory studies of the adsorption of arsenic onto iron oxides have indicated a dominance of a bidentate innerspheric complex formed between the arsenate tetrahedron

and the oxide surface (e.g. Waychunas et al. 1993). In contrast to these studies, the adsorption process at the Rötzbach and at similar natural environments occurs at very low As concentrations in the water and over much longer time.

The radial distribution functions of natural specimens have, besides the first shell of the As-O tetrahedron, substantial peaks which can be attributed to As-Fe complex formation. In most samples the As(V)-Fe distance is  $3.24 \pm 0.03$  Å with a coordination number of  $1.9 \pm 0.3$  indicating a bidentate-binuclear complex between arsenic and iron. A bidentate-mononuclear chelate complex is also detected in two samples, as was shown for synthetic As-ferrihydrite by Manceau (1995). No scorodite related structures were measured.

## 5 Conclusions

The Rötzbach site allows for investigation into how naturally occurring acidic waters, due to pyrite dissolution, are attenuated in geological time spans. This is complimentary to study mining sites with higher input functions in lesser time.

Sulphate and pH are found to control the formation of different iron minerals, the former parameters being controlled by the oxidation rates and the hydrological conditions of the discharge. The precipitation of these minerals lowers the sulphate concentration, thus allowing for the formation of Fe-(oxy)hydroxide minerals further downstream. These proton generating reactions depress the pH of the watercourse, despite the inflow of alkaline tributaries.

The data from this natural system indicates jarosite as the first secondary mineral phase to be formed, at a pH of  $< 2.5$ . This formation is typical (Jambor 2003), although the sulphate concentration measured is much lower than that measured in mine wastes (Bigham 1994). Schwertmannite also forms at lower sulphate concentrations than measured in mine wastes. It is the most widely distributed precipitate until the sulphate concentration becomes too low (downstream of point R20).

Iron minerals are strong scavengers of metals, especially the metalloid arsenic, caused by a specific adsorption process as demonstrated by EXAFS data. There is no data indicating the precipitation of ferric arsenate scorodite. Even at an As concentration as low as  $0.5 \mu\text{g L}^{-1}$ , the iron minerals contain up to  $450 \mu\text{g g}^{-1}$  As. The adsorbed As concentration can reach levels as high as  $6,000 \mu\text{g g}^{-1}$ ; that is around 150 more concentrated than the original pyrite source.

Naturally occurring acid rock drainage will be attenuated by the formation of secondary iron precipitates which decrease the concentrations of sulphates and metals. The same sequence of iron minerals is formed at sites of human activity, such as mining works, although the values of controlling parameters like sulphate are much lower at the Rötzbach site. This maybe counterbalanced by the increase in time taken to form a certain hydrogeochemical environment. The high metal loads at the scavenging minerals should be of concern whenever and wherever iron and manganese precipitates occur during the life cycle of a mining project, even when water quality is excellent.

The positive effect of secondary iron oxides to reduce metal loads from mine works produces at the same time a highly enriched solid waste. This waste is of no concern as long as the chemical environment favours the formation of the iron oxides. But, the stability of that sink should always be reviewed critically.

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